Determination of Polystyrene in GR-S Rubber*

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Synopsis — *A convenient procedure for the determination of polystyrene in GR-S is given. The method depends upon degradation of the GR-S by tert-butyl hydroperoxide in the presence of a trace of osmium tetroxide. Polystyrene is not attacked and is separated by precipitation with ethanol.*

INTRODUCTION

In the preparation of GR-S (a copolymer of butadiene and styrene) and other copolymers by emulsion polymerization, the monomers are usually mixed before they are added to the aqueous solution of soap and catalyst. In the preparation of GR-S, it is essential not to add the styrene to the aqueous solution before the addition of butadiene because styrene polymerizes much more rapidly than butadiene or a mixture of butadiene and styrene. If, in actual plant practice, the styrene is permitted to be in contact with the solution of soap and catalyst before addition of butadiene, the copolymer obtained is not pure GR-S, but a mixture of GR-S and polystyrene.

In the early days of the preparation of GR-S plant samples of low conversion were often found to have an abnormally high styrene content.[1] It was suspected that the high styrene content was due to the fact that the samples consisted of a mixture of polystyrene and GR-S. A method for the determination of polystyrene in GR-S was, therefore, needed.

In 1943 an approximate method for the determination of polystyrene in GR-S was developed in this laboratory. The method was based on the fact that the addition product of GR-S with iodine monochloride is only slightly soluble in a mixture of 25% ethanol in benzene, whereas polystyrene is completely soluble. After removal of the precipitated addition product, all the polystyrene and the fraction of the iodine monochloride addition product remaining in solution can be precipitated by the addition of a large quantity of ethanol. In order to find the polystyrene content of the weighed precipitate, it is necessary to determine the amount of the iodine monochloride addition product present, which can be done by means of an iodine analysis.

The quantity of addition product that precipitates with the polystyrene depends on the molecular-weight distribution of the former. In other words, when more material of low molecular weight is present, more addition product is not removed in the first precipitation. For this reason the method was found to be satisfactory only for the determination of relatively large amounts of polystyrene (75%) in high-conversion GR-S.

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[1] W. O. Baker, Bell Telephone Laboratories, *private communication.*

It was not suitable for polystyrene determinations in low-conversion GR-S and in high-conversion GR-S containing small amounts of polystyrene.

An attempt was then made to make use of the fact, noted in this laboratory, that the solubility of GR-S in a mixture of benzene and acetone is small, whereas polystyrene is freely soluble in such mixtures. For example, in a mixture of 80% acetone and 20% benzene, varying amounts of a low-conversion (24%) GR-S sample prepared by bottle polymerization were almost completely separated from high-conversion (80%) polystyrene. To 20 ml. of benzene solutions containing varying ratios of high-conversion polystyrene and low-conversion GR-S in a total concentration of 1%, 80 ml. of acetone was added. The precipitated GR-S polymer was filtered off and was found to contain about 1% polystyrene (from a determination of the iodine number). The filtrate was then added to a large volume of ethanol to precipitate the remaining copolymer and polystyrene. The amounts of polymer found in this second precipitation are given in Table I.

TABLE I

SEPARATION OF 24%-CONVERSION GR-S AND HIGH-CONVERSION POLYSTYRENE IN BENZENE–ACETONE (20:80)

GR-S in original mixture, %	Polystyrene in original mixture, %	Polymer not precipitated in 20:80 benzene-acetone, %
100	0	1.8 2.0
95	5	5.8 6.5
75	25	25.5 24.8
50	50	48.0 47.8

The results summarized in Table I and those of other experiments have shown, however, that the use of a benzene–acetone mixture is not suitable for a quantitative separation of GR-S from polystyrene. The reason is that GR-S contains low molecular weight fractions which are soluble in the benzene–acetone mixture. The principle of separation is mentioned here because it allows a fairly close separation of the GR-S from polystyrene without affecting either substance chemically.

The following procedure describes a possible method for the quantitative determination of polystyrene in GR-S based on the above separation. Collect quantitatively and weigh the GR-S fraction which precipitates when acetone is added to a benzene solution of the sample. This fraction is practically free of polystyrene. Precipitate the remaining copolymer and polystyrene in the benzene solution by the addition of ethanol, and weigh. From the weight of both precipitates and the unsaturation of both fractions (iodine monochloride method), the polystyrene content of the original sample can be calculated.

This method was abandoned in favor of a much simpler procedure which is described below. In brief, the new method is based upon the principle that polymer molecules (such as GR-S) containing ethylenic bonds, when dissolved in benzene, can be broken into fragments by a hydroperoxide in the presence of osmium tetroxide; polymer molecules (such as polystyrene) containing no ethylenic bonds remain unattacked. The

small fragments (aldehydes of low molecular weight) are soluble in ethanol, whereas the unattacked polystyrene is insoluble. Separation of the polystyrene, therefore, consists merely of pouring the reaction mixture (after breakdown of the polymer containing unsaturated groups) into ethanol and filtering off the polystyrene.

It is expected that the oxidation of GR-S described in this paper may be of greater importance in connection with a study of the structure of the copolymer. A quantitative determination of all the oxidation products should give complete insight into the structure of GR-S and other polymers containing unsaturated bonds. The method appears to have definite advantages over degradation by ozone. This problem will be studied further by H. A. Laitinen of the University of Illinois.

In a subsequent paper we shall describe the reactivity of polymers containing unsaturated groups with perbenzoic acid in an organic solvent and also with perbenzoic acid in the presence of a small amount of osmium tetroxide. With perbenzoic acid alone the double bonds form an oxirane ring (*i.e.*, an epoxide) whereas in the presence of osmium tetroxide, oxidation to aldehydes occurs.[2] Several analytical applications of these reactions will be described later.

REAGENTS

tert-Butyl Hydroperoxide. A mixture containing 60% *tert*-butyl hydroperoxide and 40% *tert*-butyl alcohol was obtained from Union Bay State Company, Cambridge, Massachusetts. The mixture is stable for at least several months at room temperature.[3,4]

Osmium Tetroxide Solution. 0.08 g. of osmium tetroxide was dissolved in 100 ml. of reagent-grade benzene. The solution is stable for several months if protected from light. Decomposition is indicated by the formation of a black precipitate, osmium sesquioxide or osmium dioxide.

PROCEDURE

Heat 40–50 g. of *p*-dichlorobenzene contained in a 125-ml. Erlenmeyer flask to 50–60°C. Weigh out a 0.5 to 0.6-g. sample of polymer accurately to 1 mg. and transfer it to the flask. Heat the solution to about 130°C. and maintain the temperature until the sample has dissolved. Even polymers containing gel are dissolved by this procedure. If the sample contains no gel, it will dissolve in 15–30 minutes. A hot plate, not an open flame, should be used to heat the solution. If a flame is used, the polymer will stick to the bottom of the flask due to the high temperature of the glass surface.

Cool the solution to 80–90°C. and add 10 ml. of 60% *tert*-butyl hydroperoxide. Add 1 ml. of 0.003 *M* osmium tetroxide solution in benzene. Heat the solution to 110–115°C. and keep at this temperature for 10 minutes. The solution should be perfectly clear at this point.

Cool the solution to 50–60° and add 20 ml. of benzene. Pour the solution slowly into 250 ml. of ethanol containing a few drops of concentrated sulfuric acid. Stir the mixture by means of a mechanical stirrer during this addition. Wash the flask with small portions of benzene. Stir the mixture until the polystyrene has coagulated and the solution is clear. If necessary, the solution should be allowed to stand overnight.

[2] R. Criegee, *Ann.*, 522, 75 (1936).
[3] N. A. Milas and S. Sussman, *J. Am. Chem. Soc.*, 58, 1302 (1936); *ibid.*, 59, 2345 (1937).
[4] N. A. Milas and S. A. Harris, *ibid.*, 60, 2434 (1938).

Filter the solution through a sintered glass filter,[5] which has previously been weighed with an accuracy of 1 mg., and wash with ethanol. Dry the filter at 110°C. for 4 hours. Finally cool and weigh the filter.

DISCUSSION

The following preliminary experiments led to specifications for the optimum conditions for a routine procedure.

(1) 0.5 g. of GR-S (free of polystyrene impurity) was dissolved in 50 g. of melted *p*-dichlorobenzene. The mixture was cooled to 90°C. and 10 ml. of *tert*-butyl hydroperoxide and 1 ml. of a benzene solution 0.003 *M* in osmium tetroxide were added. The temperature of the solution was maintained at 95–100° and 1-ml. aliquots were removed from time to time and added to 5 ml. of absolute ethanol. The portions taken after 1, 2, 3, 4, and 5 minutes of heating produced turbidities. The portions taken after 6 or more minutes of heating gave clear solutions when added to the ethanol. To insure a complete breakdown of GR-S in the routine procedure, a temperature of 110–115° for 10 minutes has been specified.

(2) Similar experiments were made in which varying amounts of osmium tetroxide were used. Because of the fact that osmium tetroxide catalyzes the decomposition of the hydroperoxide and also because of the high price of osmium tetroxide, a higher concentration of the catalyst than is given in the procedure is not recommended. If no osmium tetroxide is added, the breakdown of the GR-S is not apparent even after a long period of heating at 110°.

(3) 0.5 g. of GR-S was treated according to the procedure given in (1). The reaction mixture was poured into 70% ethanol–30% water. A perfectly clear solution resulted, indicating that the aldehyde fragments are small.

(4) Mixtures of GR-S and polystyrene (prepared by emulsion polymerization) were analyzed by the procedure given above. The results are reported in Table II.

TABLE II

DETERMINATION OF POLYSTYRENE IN POLYSTYRENE–GR-S MIXTURES

Polystyrene taken, mg.	GR-S taken, mg.	Polystyrene found, mg.
0	500	0
10	500	9.9
200	300	201.4
500	0	499.0

TABLE III

DETERMINATION OF POLYSTYRENE IN PLANT SAMPLES

Polymer	Conversion, %	Polystyrene found, %	
		By osmium tetroxide method	By iodine monochloride method
17 P 35 A 2-b	12	0.3	5
17 P 42 A 1-b	12	2.8	14
Blend B-f	72	0.0	0
17 P 41 A 2-b	16	27.0	33

[5] A Pyrex filter of coarse grade is satisfactory.

DETERMINATION OF POLYSTYRENE IN GR-S RUBBER

The procedure has been used for the determination of polystyrene in GR-S samples prepared in the government pilot plant of the University of Akron. In the preparation of samples, the polymerization was started after the addition of styrene, but before the addition of butadiene. As was expected, these samples were found to contain polystyrene. In the preparation of sample "Blend B-f" the charges were prepared in such a way that polymerization of styrene could not occur before the copolymer began to form.